



Synthesis of synergetic phosphorus and cyano groups ($-\text{C}\equiv\text{N}$) modified $\text{g-C}_3\text{N}_4$ for enhanced photocatalytic H_2 production and CO_2 reduction under visible light irradiation

Xiaolei Liu^a, Peng Wang^{a,*}, Huishan Zhai^a, Qianqian Zhang^a, Baibiao Huang^{a,*}, Zeyan Wang^a, Yuanyuan Liu^a, Ying Dai^b, Xiaoyan Qin^a, Xiaoyang Zhang^a

^a State Key Lab of Crystal Materials, Shandong University, Jinan 250100, China

^b School of Physics, Shandong University, Jinan, 250100, China

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ABSTRACT

Graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) has become an attractive photocatalyst for solar energy conversion owing to its numerous advantages. Due to insufficient solar-light absorption and fast photogenerated carriers recombination, the photocatalytic activity of traditional $\text{g-C}_3\text{N}_4$ material is unsatisfactory. In this work, P element and cyano groups ($-\text{C}\equiv\text{N}$) incorporated into the $\text{g-C}_3\text{N}_4$ framework is successfully fabricated by heat treatment of the mixed $\text{g-C}_3\text{N}_4$ and NaH_2PO_2 . The cyano groups ($-\text{C}\equiv\text{N}$) originated from the de-protonation of $-\text{C}-\text{NH}_2$ can enhance the light absorption and act as strong electron-withdrawing groups, which can promote the efficient separation of photo-generated electron-hole pairs. The P element doping can enhance the visible light absorption, shorten the band gap and suppress the recombination of photo-induced carriers. The synergistic effect of $-\text{C}\equiv\text{N}$ functional groups and P element doping results in a 6.7 times enhanced photocatalytic H_2 production activity and 1.58 times enhanced photocatalytic CO_2 reduction activity than that of pristine $\text{g-C}_3\text{N}_4$. Experimental analysis indicates that the enhanced photocatalytic performance is mainly attributed to the enhanced light absorption and charge separation. Our work provides a new thought to design other high performance and low-cost $\text{g-C}_3\text{N}_4$ -based photocatalytic materials for solar energy conversion.

1. Introduction

The excessive consumption of fossil fuels continues to deepen the worldwide energy crisis, accompanied by the release of a considerable amount of CO_2 , which results in green-house effect and environmental pollution [1,2]. Photocatalytic H_2 production from water and photocatalytic conversion CO_2 to CO or hydrocarbon fuels are very promising ways to convert solar energy into other types of clean chemical fuels and reduce green-house effect [3,4]. Therefore, development and design of high efficient, low-cost and eco-friendly photocatalysts have become the main research hotspots in photocatalytic fields. Recent years, graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) as a polymeric-type semiconductor has received tremendous attention in photocatalytic fields owing to its low cost, peculiar thermal and chemical stability, non-toxicity and suitable band structure [5,6]. Therefore, $\text{g-C}_3\text{N}_4$ has been recognized as a promising photocatalyst for solar energy conversion, such as photocatalytic H_2 production and CO_2 reduction [7–11].

$\text{g-C}_3\text{N}_4$ with band gap energy of 2.7 eV can be easily synthesized by

thermal polymerization melamine, dicyanamide, urea or thiourea. The conduction band bottom of $\text{g-C}_3\text{N}_4$ is located at about -1.1 eV (vs. NHE), which is negative sufficiently for photocatalytic H_2 production and CO_2 reduction [12]. Although $\text{g-C}_3\text{N}_4$ has so many advantages, its photocatalytic activity is still low due to the limited visible light absorption, small specific surface area and high recombination rate of photo-generated carriers. Thus, extensive strategies have been developed to improve the photocatalytic behavior of $\text{g-C}_3\text{N}_4$, such as nanostructure engineering [13–18], doping with heteroatoms to extend light absorption range and promote the separation efficiency of photo-generated electron-hole pairs [19–21], being exfoliated to a few layers [22,23], heterostructure construction [24–26] or being decorated with co-catalyst [27–32]. Particularly, the introduction of defects or doping with heteroatoms into the $\text{g-C}_3\text{N}_4$ framework has been found to be effective ways to improve the photocatalytic activity [19,33–35]. Doping with heteroatoms or introducing defects in the tri-s-triazine repeating units of $\text{g-C}_3\text{N}_4$ can modify the electronic structure and band gap, also act as reactive sites for photocatalytic reaction. In view of these advantages,

* Corresponding authors.

E-mail addresses: pengwangicm@sdu.edu.cn (P. Wang), bbhuang@sdu.edu.cn (B. Huang).

introducing defects and heteroatoms together in g-C₃N₄ may bring better performance than alone. But the current researches in g-C₃N₄ are always focusing on introducing defects or heteroatoms alone, and as for defects studies, a relatively high reaction temperature and reducing atmosphere (like H₂ and NH₃) are both necessary to realize the incorporation of defect into g-C₃N₄ structure [36,37]. Therefore, simple and effective methods are required toward the synthesis of both defects and heteroatoms modified g-C₃N₄.

In this research, we present a simple and effective method to synthesize both defect and heteroatoms modified g-C₃N₄ through second calcination of the mixed g-C₃N₄ and NaH₂PO₂ under inert atmosphere. During calcination, NaH₂PO₂ decomposes to gaseous PH₃ and solid-state Na₂HPO₄ at temperature greater than 150 °C according to the reaction: $2\text{NaH}_2\text{PO}_2(\text{s}) \xrightarrow{\Delta} \text{PH}_3(\text{g}) \uparrow + \text{Na}_2\text{HPO}_4(\text{s})$ [38]. Solid-state Na₂HPO₄ can react with g-C₃N₄ to produce cyano terminal C≡N groups, and gaseous PH₃ can dope P element into g-C₃N₄ structure. The formation of –C≡N functional groups can not only enhance the light absorption but also act as strong electron-withdrawing groups in g-C₃N₄ to promote the efficient separation of photogenerated carriers [33,42], the doping of P heteroatom into g-C₃N₄ structure can extend the light absorption, increase the electric conductivity and suppress the recombination of photo-generated electron–hole pairs [39]. The synergistic effect of –C≡N functional groups and doping of P heteroatom results in a 6.7 times enhanced photocatalytic H₂ production activity and 1.58 times enhanced photocatalytic CO₂ reduction activity than that of pristine g-C₃N₄. This work provides a simple and effective route to realize both defects and heteroatoms modified g-C₃N₄, the enhanced light absorption and efficient separation of photo-generated carriers are benefit for high efficient solar energy conversion.

2. Experimental section

2.1. Synthesis of pristine g-C₃N₄

Pristine g-C₃N₄ was prepared by traditional thermal polycondensation. Briefly, 6 g of urea and 6 g of dicyandiamide were grounded in an agate mortar for 20 min. Then, the mixture was calcined at 550 °C in a muffle furnace for 4 h using a heating rate of 5 °C min^{−1} in air. After cooling naturally, the yellow product was grounded for 30 min to obtain a powder sample. The obtained product was 4.8 g and the yield was 40%.

2.2. Preparation of phosphorus and cyano groups (–C≡N) modified g-C₃N₄

Briefly, the as-prepared g-C₃N₄ (0.4 g) was mixed with NaH₂PO₂ (0.2 g) at a weight ratio of 2:1, grounded in a mortar sufficiently, and then calcined in a tube furnace under Ar atmosphere at different temperatures (300 °C, 350 °C, 400 °C, 425 °C, 450 °C and 500 °C) for 60 min using a heating rate of 10 °C min^{−1}. Residual PH₃ was very dangerous, so strong oxidizing sodium hypochlorite solution (1 mol/L) was used to absorb the residual PH₃ at the end of the vent. After cooling naturally, the resultant products were washed with water, NaOH (0.1 mol/L), HCl (0.1 mol/L) and water again to remove any unreacted and potentially detrimental surface species. The achieved products were denoted as g-C₃N₄-x, x indicated the heating temperature. By contrast, the preparation process of g-C₃N₄ treated by Na₂HPO₄ was the same as g-C₃N₄ treated by NaH₂PO₂ except replacing NaH₂PO₂ by Na₂HPO₄.

2.3. Material characterization

X-ray diffraction patterns (XRD) were recorded on a Bruker AXS D8 diffractometer equipped with Cu Kα radiation (λ = 0.154056 nm). Diffuse reflectance UV–vis absorption spectroscopy was recorded using Shimadzu UV-2550 spectrophotometer, with BaSO₄ performing

as a reference. Morphologies and microstructures of the products were characterized by scanning electron microscopy (Hitachi S-4800) equipped with an Energy Dispersive Spectrometer (EDS) and transmission electron microscopy (JEOL JEM-2100F). X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific Escalab 250 spectrometer) with monochromatized Al Kα excitation was used to analyze quantitatively the chemical composition of the products and C 1 s (284.8 eV) was used to calibrate the peak positions. Fourier-transform infrared (FTIR) spectra were recorded using the FT-IR spectrometer (Nicolet Nexus 670). The PL measurement was analyzed on a Hitachi F-4500 fluorescence spectrophotometer at room temperature and obtained with excitation wavelength at 360 nm. The time resolved fluorescence spectra were recorded at 460 nm using a 377.8 nm excitation by Edinburgh FLS920 PL, decay curves were fitted by using a biexponential decay function to obtain deconvolution of the instrument response function. The Brunauer–Emmett–Teller (BET) specific surface area was measured by a Micromeritics ASAP 2020 apparatus. Isotopic experiment was performed using ¹³CO₂ (purity: 99%), and the produced CO was analyzed by gas chromatography-mass spectrometry (GC–MS).

2.4. Photoelectrochemical measurement

Photocurrent response and electrochemical impedance spectroscopy (EIS) measurements were measured by a Princeton Applied Research EG&G 263 A electrochemical analyzer using a standard three-electrode mode with 0.2 M Na₂SO₄ (pH = 6.8) solution as the electrolyte, the catalyst-coated FTO glass as the working electrode, a Pt sheet as the counter electrode and Ag/AgCl as the reference electrode. The light source was a 300 W Xe arc lamp coupled with an AM1.5 global filter. The photocurrent response was measured at 1.0 V. To prepare the working electrodes, 50 mg of the as-prepared samples were dispersed in absolute ethanol and grounded for 30 min, the suspension was spin-coated on cleaned fluorine doped tin oxide (FTO) glass and then calcined at 450 °C for 60 min in a muffle furnace.

2.5. Photocatalytic test

Photocatalytic hydrogen production was performed in a Pyrex top-irradiation reaction vessel connected to a glass closed gas circulation system and kept at 15 °C during reaction. 100 mg of catalyst powder was well dispersed in a 100 mL mixed solution containing triethanolamine (10 vol.%) as a sacrificial agent. 1 wt% Pt was photo-deposited on the catalysts through photo-reduction of H₂PtCl₆ dissolved in the reactant solution. The system was evacuated several times to remove air completely and then irradiated by a 300 W Xe lamp equipped with a 420 nm cut-off filter (λ ≥ 420 nm) as the light source. The distance between the light source and the solution was about 14 cm, and the average power energy density of the irradiation was about 200 mW/cm² measured by PL–MW2000 spectroradiometer (PerfectLight, China). The gas production in the reaction system was sampled and measured with a gas chromatograph (GC-7806, Shiweipx). In order to investigate the stability of the product, cycling experiment was taken out. The detailed procedures were as follows: after irradiation for 3 h, the produced H₂ was removed by a vacuum pump. Then, the next cycle began under the same condition. And the action spectra were measured under the same conditions with band-pass monochromatic filters centered at 420, 450, 520 and 600 nm, respectively. The quantum efficiency (QE) for H₂ production was measured with a 300 W Xe-lamp equipped with a 420 nm (± 10 nm) monochromatic filter as the light source. The irradiation area was 4 cm² and the average energy density was 55 mW/cm². The QE was calculated using the following equation:

$$QE = \frac{2 \times \text{thenumber of evolved hydrogen}}{\text{thenumber of incident photons}} \times 100\%$$

Photocatalytic CO₂ reduction was performed in a 250 mL Pyrex top-irradiation reactor at ambient temperature and atmospheric pressure.

The opening of the reactor was sealed with silicone rubber plug to form a closed system, and a 300 W Xe lamp equipped with a 420 nm cut-off filter ($\lambda \geq 420$ nm) as the light source. Before reaction, 1 wt% Au was deposited on the catalysts through chemical reduction of HAuCl₄ using NaBH₄ as reductant. 100 mg of as-prepared product was well dispersed in a 100 mL solution containing 1 M NaHCO₃, and the system was bubbled with high purity CO₂ for 10 min. And the contrast experiment was carried out without adding NaHCO₃ and bubbling high purity CO₂, before irradiation, the system was vacuumed by pump and high purity Ar gas was bubbled for 30 min to ensure that almost no CO₂ took part in the reaction. The gas production in the reaction system was sampled and measured with a gas chromatograph (GC-7920, CEAULIGHT, Beijing) equipped with a flame ionized detector. In order to study the stabilities of the products, cycling experiment was taken out. The detailed procedures were as follows: after irradiation for 3 h, the produced CO was removed by blowing high purity CO₂. Then, the next cycle began under the same condition. And the isotopic experiment was performed using ¹³CO₂ (purity: 99%), and the produced CO was analyzed by gas chromatography-mass spectrometry (GC-MS).

3. Results and discussion

The phase structures of as-prepared products were identified by powder X-ray diffraction analysis. As shown in Fig. 1, the pristine g-C₃N₄ exhibits two distinct characteristic peaks at 13.1° and 27.4°, respectively. The minor diffraction peak at 13.1° is corresponded to the (1 0 0) plane and ascribed to the in-plane structural packing motif of tri-s-triazine [40]. The high-angle diffraction peak at 27.4° is the characteristic peak of an interlayer stacking of conjugated aromatic systems, which is indexed to the (0 0 2) plane for graphitic materials [41]. All of the XRD patterns of g-C₃N₄ treated with NaH₂PO₂ at different temperatures are very similar to that of pristine g-C₃N₄, indicating that the basic crystal structure of g-C₃N₄ is preserved with NaH₂PO₂ treatment. However, both the diffraction peaks at 13.1° and 27.4° are broadened and gradually weakened, suggesting that the ordered and periodic structures within the framework of g-C₃N₄ are broken during the heat treatment with NaH₂PO₂.

The chemical structures of as-prepared products were analyzed by Fourier transform infrared (FTIR) spectra, as shown in Fig. 2. In Fig. 2a, the pristine g-C₃N₄ shows a spectrum with typical characteristic peaks: the peak at 810 cm⁻¹ is the characteristic breathing mode of s-triazine ring system, the peaks located between 1000 and 1800 cm⁻¹ originate from the typical stretching vibration modes of C=N and C-N heterocycles, while multiple broad peaks in 3000–3500 cm⁻¹ region are

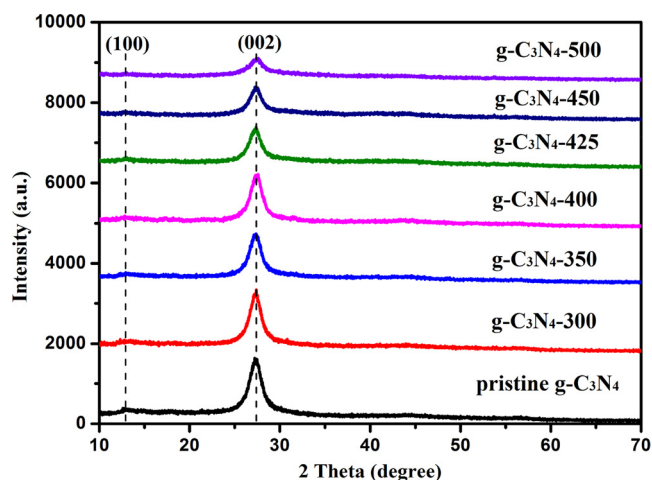


Fig. 1. XRD patterns of pristine g-C₃N₄ and g-C₃N₄ after heat treatment with NaH₂PO₂ at different temperatures (300 °C, 350 °C, 400 °C, 425 °C, 450 °C and 500 °C).

ascribed to N–H stretching vibrations [22]. For the g-C₃N₄ products after heat treatment with NaH₂PO₂ at different temperatures, a new vibration band at 2180 cm⁻¹ appears, belonging to an asymmetric stretching vibration of cyano groups (–C≡N) [33,42,43]. The vibration peak intensity of cyano group increases and the peak intensity of N–H stretching vibrations decreases gradually with the heating temperature increasing, which may prove that the cyano groups originate from the de-protonation of –C–NH₂. The intensity of the peak at 810 cm⁻¹ decreases gradually with the heating temperature increasing, suggesting that the s-triazine ring system is destroyed, which is consistent with the XRD result. During heating, NaH₂PO₂ decomposes into gaseous PH₃ and solid-state Na₂HPO₄. In Fig. 2 b, the FTIR spectrum of g-C₃N₄ after heat treatment at 425 °C alone in Ar atmosphere shows no difference with pristine g-C₃N₄. However, the cyano groups (–C≡N) appears in the FTIR spectra of g-C₃N₄ after heat treatment with Na₂HPO₄ at different temperatures, suggesting that the appearance of cyano groups may be caused by Na₂HPO₄.

Further detailed surface chemical status and chemical compositions of pristine g-C₃N₄ and g-C₃N₄ after heat treatment with NaH₂PO₂ for 1 h at 425 °C were analyzed with X-ray photoelectron spectroscopy (XPS) measurements. As compared in Fig. 3a, XPS survey spectra of both pristine g-C₃N₄ and g-C₃N₄-425 contain three sharp peaks at 288.2, 398.72 and 532 eV, which are respectively assigned to C 1 s, N 1 s, and O 1 s signals. The O 1 s signal may be from the absorbed H₂O and CO₂ on the surface of the products. In order to find the difference between pristine g-C₃N₄ and g-C₃N₄-425, the corresponding high resolution XPS spectra of C, N and P are shown in Fig. 3b–d. For the pristine g-C₃N₄, the high resolution C 1 s spectrum is fitted into three peaks, the peak centered at 284.8 eV is assigned to carbon impurities, the main peak centered at 288.2 eV is ascribed to sp²-bonded carbon of N=C–N in the aromatic ring and the peak centered at 286.27 eV is ascribed to the sp² C atoms in the aromatic ring attached to the –NH₂ group [5]. The high resolution N 1 s spectrum is also fitted into three peaks, which are located at 398.72, 400.22, and 401.43 eV for sp²-hybridized nitrogen (N=C=N), tertiary nitrogen (N–(C)₃), and terminal amino groups (C–NH), respectively [2]. As for g-C₃N₄ after heat treatment with NaH₂PO₂ for 1 h at 425 °C, a little difference is appeared relative to the pristine g-C₃N₄ that the peak at 286.15 eV for the sp² C atoms in the aromatic ring attached to the –NH₂ group and the peak at 401.29 eV for terminal amino groups (C–NH) are a little deflected. Combining this tiny variation, we speculate that the cyano groups (–C≡N) originate from de-protonation of –C–NH₂ by oxidizing Na₂HPO₄. This result agrees well with the FTIR result. No P element is detected in the pristine g-C₃N₄, but in Fig. 3d, obvious P element is detected in the g-C₃N₄-425 product. The peak of P2p binding energy is centered at 133.9 eV, which is typical for the P–N bond (P–C bonding would be 1–2 eV lower) [39,40]. So the P element is doped into the g-C₃N₄ system, the weight ratio of P provided by EDS result is about 0.18%, the detailed information can be seen in Section 4, supporting information (Table S1).

The optical absorption properties of the prepared products were studied by UV–vis diffuse reflection spectra. As shown in Fig. 4a, the pristine g-C₃N₄ shows the typical absorption edge at about 450 nm and g-C₃N₄ heating without NaH₂PO₂ at 425 °C in Ar atmosphere shows only a little variation. However, when the g-C₃N₄ is treated with NaH₂PO₂ at different heating temperatures (300 °C, 350 °C, 400 °C, 425 °C, 450 °C and 500 °C) in Ar atmosphere, the gradual red-shift to longer wavelength is observed following the enhanced heating temperature. Consistent with the absorption results, the colour of the products suffers a corresponding change from yellow to brown as the treatment temperature increases (more detailed information can be seen in Fig. S2). The significant red-shift of the absorption wavelength indicates that the products can absorb more solar energy, which is benefit for the photocatalytic activity. And the enhanced light absorption may derive from the P element doping and the formation of cyano groups (–C≡N). The influence in the light absorption of cyano groups

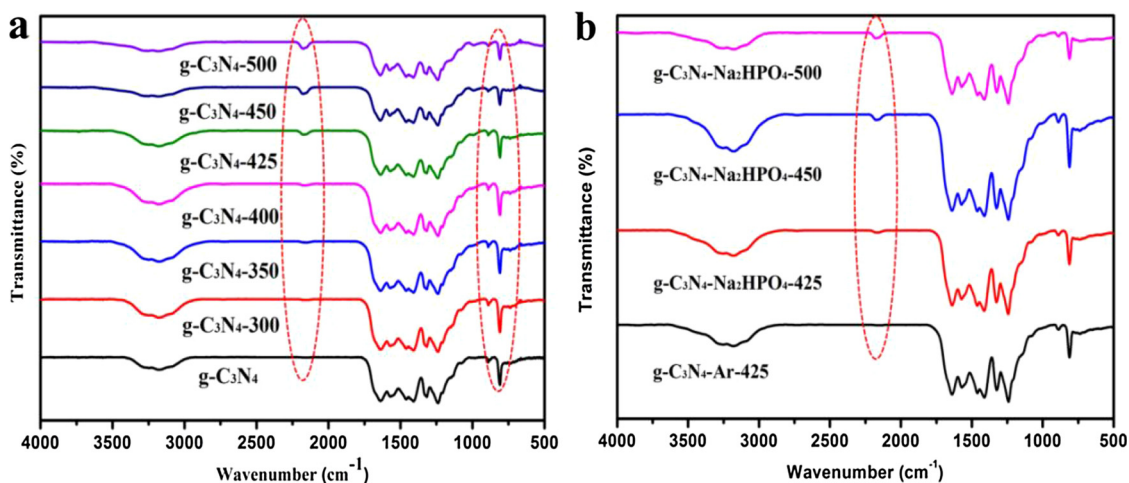


Fig. 2. (a) The FTIR spectra of pristine $g\text{-C}_3\text{N}_4$ and $g\text{-C}_3\text{N}_4$ after heat treatment with NaH_2PO_2 for 1 h at different temperatures (300 °C, 350 °C, 400 °C, 425 °C, 450 °C and 500 °C), (b) The FTIR spectra of $g\text{-C}_3\text{N}_4$ after heat treatment at 425 °C alone in Ar atmosphere and $g\text{-C}_3\text{N}_4$ after heat treatment with Na_2HPO_4 for 1 h at different temperatures (425 °C, 450 °C and 500 °C).

($-\text{C}\equiv\text{N}$) can be seen in Section 3 (Fig. S3), supporting information. Fig. 4 b shows the calculated band gaps for $g\text{-C}_3\text{N}_4$ and $g\text{-C}_3\text{N}_4\text{-X}$ (X means the temperature of heat treatment). The band gaps of the samples determined from the Kubelka–Munk transformation are reduced

from 2.60 ($g\text{-C}_3\text{N}_4$), to 2.54 ($g\text{-C}_3\text{N}_4\text{-300}$), to 2.46 ($g\text{-C}_3\text{N}_4\text{-350}$), to 2.28 ($g\text{-C}_3\text{N}_4\text{-400}$), to 2.22 ($g\text{-C}_3\text{N}_4\text{-425}$), to 2.20 ($g\text{-C}_3\text{N}_4\text{-450}$) to 2.18 eV ($g\text{-C}_3\text{N}_4\text{-500}$).

The photocatalytic activities of as-prepared products were evaluated

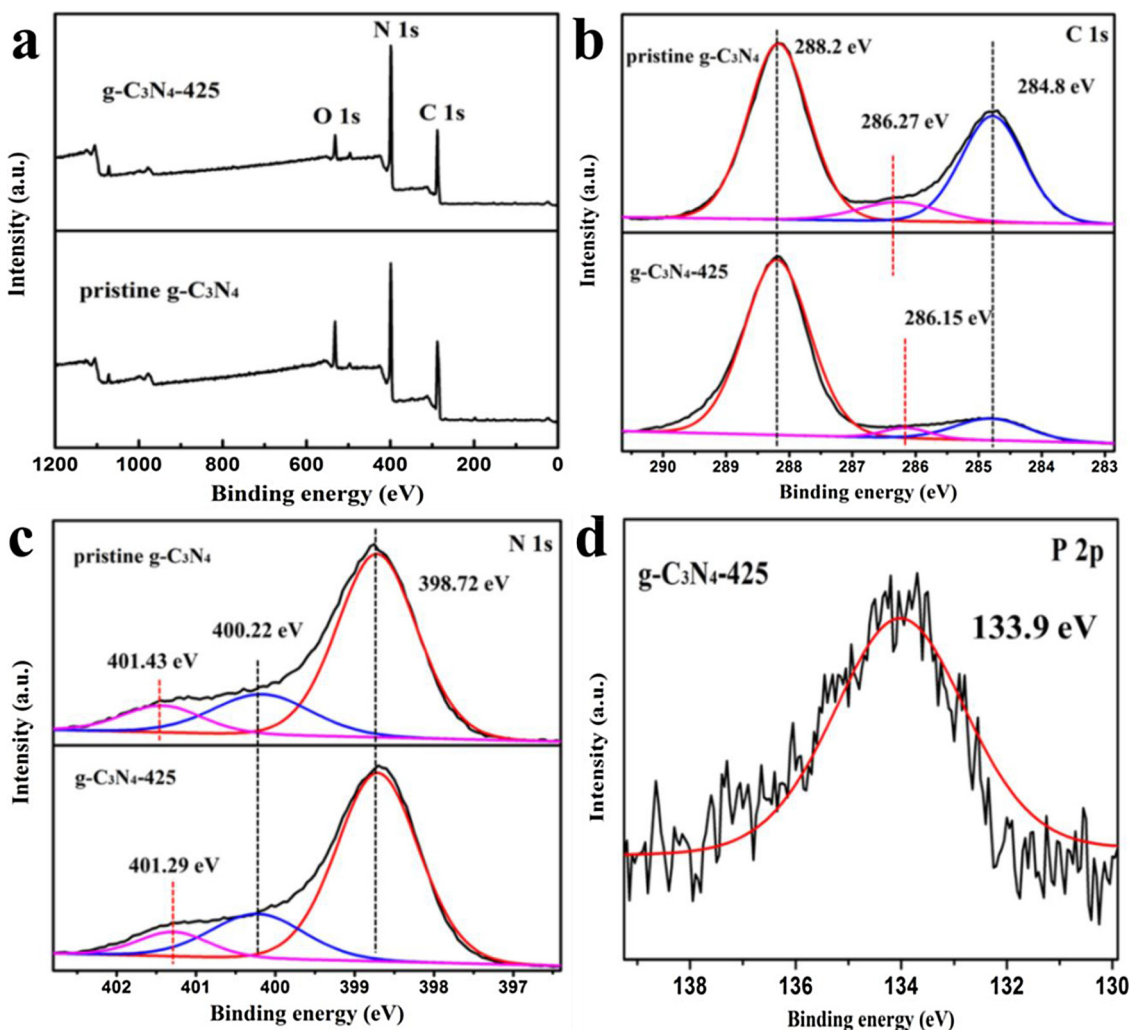


Fig. 3. (a) XPS survey spectra, (b–c) high-resolution XPS spectra of C 1 s region and N 1 s region for pristine $g\text{-C}_3\text{N}_4$ and $g\text{-C}_3\text{N}_4\text{-425}$, respectively, (d) high-resolution XPS spectrum of P 2 p for $g\text{-C}_3\text{N}_4\text{-425}$.

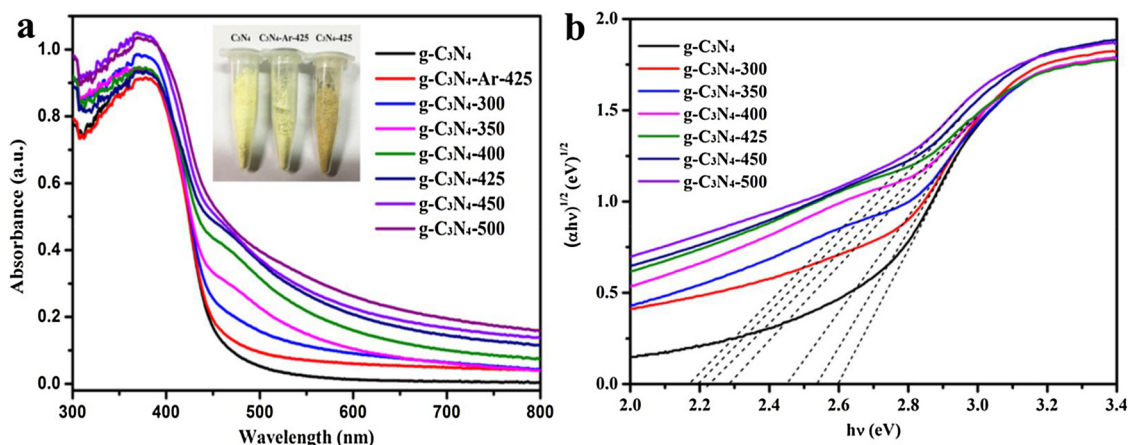


Fig. 4. (a) The UV-vis diffuse reflectance spectra of pristine g-C₃N₄, g-C₃N₄ heated at 425 °C in Ar atmosphere alone and g-C₃N₄ heated with NaH₂PO₂ at different temperatures (300 °C, 350 °C, 400 °C, 425 °C, 450 °C and 500 °C) in Ar atmosphere, (b) the calculated band gaps for g-C₃N₄ and g-C₃N₄-X (X means the temperature of heat treatment).

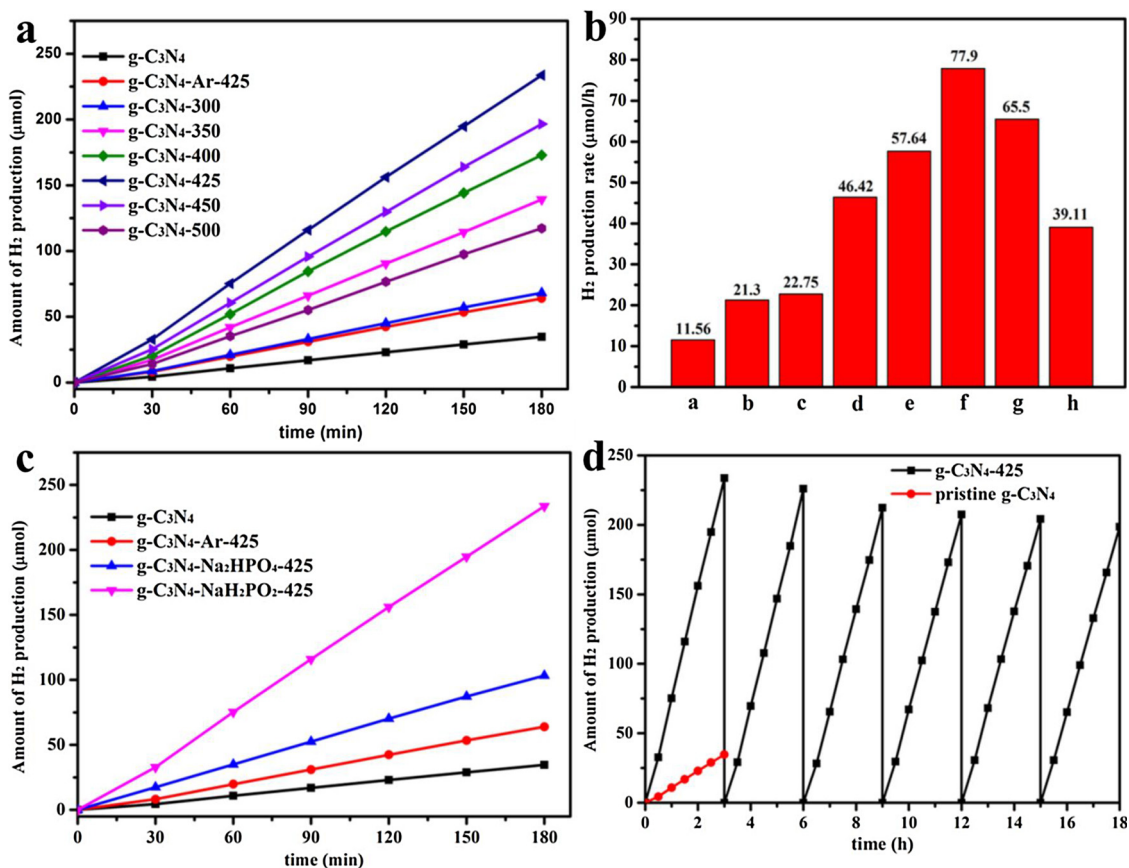


Fig. 5. (a) Time courses of H₂ production for pristine g-C₃N₄, g-C₃N₄ heated without NaH₂PO₂ at 425 °C in Ar atmosphere and g-C₃N₄ heated with NaH₂PO₂ at different temperatures in Ar atmosphere, (b) photocatalytic hydrogen production rates for the as-prepared products, a (pristine g-C₃N₄), b (g-C₃N₄-Ar-425), c (g-C₃N₄-300), d (g-C₃N₄-350), e (g-C₃N₄-400), f (g-C₃N₄-425), g (g-C₃N₄-450), h (g-C₃N₄-500), (c) comparison of photocatalytic H₂ production activities of pristine g-C₃N₄, g-C₃N₄-Ar-425, g-C₃N₄-Na₂HPO₄-425 and g-C₃N₄-NaH₂PO₂-425, (d) photocatalytic H₂ production curve of pristine g-C₃N₄ and cyclic photocatalytic H₂ production curves for the g-C₃N₄-425 sample.

by H₂ production from water and CO₂ reduction. The photocatalytic H₂ production activities of all as-prepared products were evaluated under visible-light irradiation ($\lambda \geq 420$ nm) using 1.0 wt % Pt as cocatalyst and triethanolamine as scavenger. Fig. 5a–b are a typical time course of hydrogen production and photocatalytic hydrogen production rates for pristine g-C₃N₄, g-C₃N₄ heated without NaH₂PO₂ at 425 °C in Ar atmosphere and g-C₃N₄ heated with NaH₂PO₂ at different temperatures in Ar atmosphere. Pristine g-C₃N₄ shows a low photocatalytic H₂

production rate (11.56 μmol/h), treating g-C₃N₄ with NaH₂PO₂ indeed enhances the activity. The hydrogen production rate gradually increases with the increased heating temperature from 300 °C to 425 °C. When the heating temperature rises to 425 °C, the highest hydrogen production rate is 77.9 μmol/h, which is nearly 6.7 times higher than that of pristine g-C₃N₄. In addition, the apparent quantum efficiency for H₂ production is 1.3% under 420 nm monochromatic irradiation. Further increasing the temperature, the photocatalytic performance

gradually weakens but still superior to the untreated g-C₃N₄, this could be attributed to the over-introduction of defects and structural damages. To further understand the reason for the increase in H₂ production, comparative test can be seen in Fig. 5c. G-C₃N₄ heated at 425 °C in Ar atmosphere alone shows a little increase in H₂ production, which is consistent with previous reports [34]. The H₂ production activity of g-C₃N₄ heated at 425 °C with Na₂HPO₄ is higher than that of g-C₃N₄ heated at 425 °C in Ar atmosphere alone, but still lower than that of g-C₃N₄ heated at 425 °C with NaH₂PO₂. The cyano groups (–C≡N) is produced by the treatment of oxidizing Na₂HPO₄, the implantation of –C≡N groups as strong electron-withdrawing groups into the structure of g-C₃N₄ can effectively promote the separation of the photo-generated carriers. P element doping can improve the light absorption, decrease the band gap energy and increase the electric conductivity [39]. Both the cyano groups (–C≡N) and P element are introduced into the g-C₃N₄ system, which can further improve the H₂ production activity due to the synergistic effect. Stability is a very crucial criterion for practical application of photocatalyst, the photocatalytic stability of the optimized photocatalyst was evaluated by cycling experiments under prolonged visible light illumination duration of 18 h. As shown in Fig. 5d, the photocatalytic performance remains stable after six-round cycles, no obvious decrease in H₂ production rate is detected, indicating the high stability for photocatalytic H₂ production. In the process of practical application, AM1.5 is always adopted as light source in photocatalysis. The hydrogen production rate of g-C₃N₄-425 is 137.56 μmol/h under standard solar simulator (AM 1.5) irradiation, the detailed result can be seen in section 6, supporting information. Fig. 6a gives the action spectra (wavelength dependent) of H₂ production of 1.0 wt% Pt/g-C₃N₄ under various monochromatic light irradiations (left axis). As can be seen, the variation tendency of H₂ production is similar to the UV/Vis light absorption spectrum (right axis). As we all know, g-C₃N₄ obtained by urea precursor has superior performance than other precursor due to their large specific surface area. In order to further prove the universality of treatment method, we treated the g-C₃N₄ obtained by urea precursor with the same method. The photocatalytic H₂ production tests are carried out under the same condition, Fig. 6b shows the comparison result of H₂ production. The hydrogen production rate of g-C₃N₄ (precursor: urea) and g-C₃N₄-425 (precursor: urea) are 32 and 197.45 μmol/h, respectively. After heat treatment with NaH₂PO₂, the photocatalytic H₂ production performance gets improved about 6.17 times. In addition, the apparent quantum efficiency for H₂ production is 3.67% under 420 nm monochromatic irradiation. The detailed synthetic procedure, optical absorption properties and SEM images can be seen in section 10, supporting information.

In order to further verify the enhanced photocatalytic activity, photocatalytic CO₂ reduction was performed under visible-light irradiation (λ ≥ 420 nm) using 1.0 wt % Au as cocatalyst. No CO is found

without light irradiation or photocatalyst. From Fig. 7, CO is the main product and CH₄ is negligible in this experiment. No other by-products (e.g. CH₃OH, formic acid, etc.) formed. It is difficult to accumulate multiple electrons to produce CH₄ molecule (eight electrons) and CH₃OH molecule (six electrons), while only two electrons are needed for each CO molecule. And there are many reports that Au as cocatalyst exhibits good selectively for CO production during the photocatalytic CO₂ reduction. So the conversion of CO₂ to CO is a more dynamically favorable process during the photo-reduction. In order to confirm the source of CO, the contrast experiment was carried out without adding NaHCO₃ and bubbling high purity CO₂, before irradiation, the system was vacuumized by vacuum pump and high purity Ar gas was bubbled for 30 min to ensure almost no CO₂ in the system. In Fig. 7a, only a little produced CO was detected from both pristine g-C₃N₄ and g-C₃N₄-425 systems during the irradiation. The CO might come from tiny self-decomposition of g-C₃N₄ during the irradiation. When NaHCO₃ and CO₂ were introduced into the systems, the CO yield increased a lot. The CO yield of pristine g-C₃N₄ is 0.721 μmol/g, whereas the CO yield of g-C₃N₄-425 is 1.135 μmol/g after three hours' irradiation. Obviously, the photocatalytic activity of g-C₃N₄-425 is better than that of pristine g-C₃N₄. The stabilities of pristine g-C₃N₄ and g-C₃N₄-425 were evaluated by cycling experiments. As shown in Fig. 7b, after the first three hours' irradiation, the CO yield decreases obviously, then, the performance decreases slowly in the nest cycles. The drop in performance may result from tiny self-decomposition. The sample after cycles in CO₂ reduction was characterized by XPS, the peak intensity of P in the sample after cycles in CO₂ reduction reduced, the detailed results were shown in section 5, supporting information. But the photocatalytic activity of g-C₃N₄-425 is still better than that of pristine g-C₃N₄ during the cycling experiment. Isotopic experiment was performed using ¹³CO₂ (purity: 99%) to further prove the source of CO, and the produced CO was analyzed by gas chromatography-mass spectrometry (GC-MS). The detailed result can be seen in section 9, supporting information.

The morphology and microstructures of pristine g-C₃N₄ and g-C₃N₄-425 are investigated by SEM and TEM. As shown in Fig. 8a and b, the SEM image of g-C₃N₄-425 exhibits the similar morphology with pristine g-C₃N₄, indicating that heated with NaH₂PO₂ at 425 °C doesn't affect the main morphology and structure. In Fig. 8c and d, both pristine g-C₃N₄ and g-C₃N₄-425 exhibit the typical two-dimensional structure consisting of multi-layer nanosheets. Importantly, it can be found that g-C₃N₄-425 possesses more pores in the layered structure as compared to pristine g-C₃N₄. The nano-porous structure is benefit for the photocatalytic activities. The BET surface areas of pristine g-C₃N₄ and g-C₃N₄-425 were obtained by the nitrogen adsorption-desorption, the BET surface areas of g-C₃N₄-425 was 30.14 m²/g which was a little greater than pristine g-C₃N₄ whose BET surface areas was 27.69 m²/g, the BET surface areas changed very little. So the enhancement of

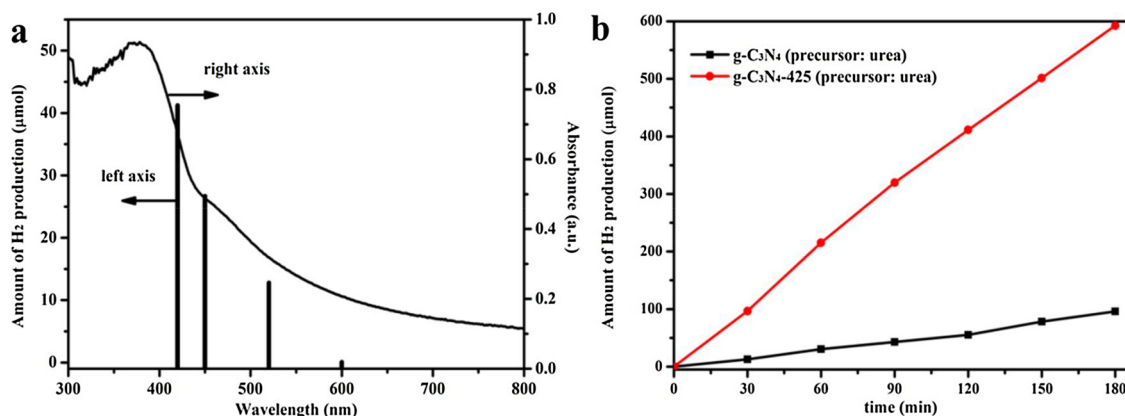


Fig. 6. (a) The action spectra (wavelength dependent) of H₂ production using 1.0 wt% Pt/g-C₃N₄-425 (left axis) and UV/Vis light absorption spectrum of g-C₃N₄-425 (right axis), (b) comparison of photocatalytic H₂ production activities of g-C₃N₄ (precursor: urea) and g-C₃N₄-425 (precursor: urea).

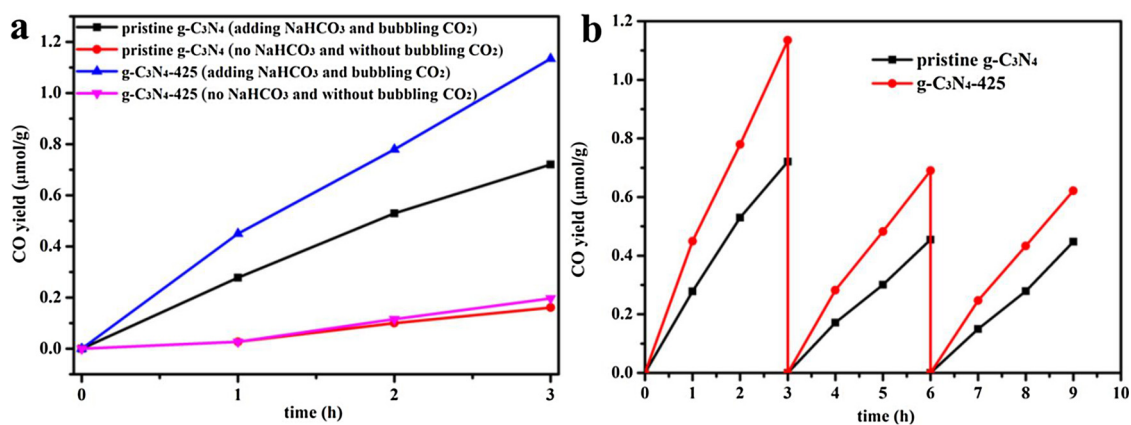


Fig. 7. (a) Time courses of CO production for pristine g-C₃N₄ and g-C₃N₄-425 with and without adding NaHCO₃ and bubbling high purity CO₂, (b) cyclic photocatalytic CO production curves for the g-C₃N₄-425 and pristine g-C₃N₄ samples.

photocatalytic H₂ production and CO₂ reduction are not just due to the weak increased BET surface areas. The STEM image of g-C₃N₄-425 and the corresponding EDS mappings of elemental C, N and P are shown in Fig. 9. In Fig. 9a, g-C₃N₄-425 exhibits the two-dimensional layer structure. The mixed EDS mappings of elemental C, N and P are shown in Fig. 9b, the red dots represent the elemental C, the green dots represent the elemental N and the blue dots represent the elemental P. The EDS mappings of C, N and P are presented in Fig. 9c–e, respectively. This result proves that P elemental presents in the g-C₃N₄ system uniformly.

The effective generation and instant separation of photo-excited charge carriers are crucial for the photocatalytic reactions [44]. The room-temperature PL and TRPL (the time resolved fluorescence) spectra were measured to characterize the recombination rate and lifetime of photo-generated electrons and holes. As shown in Fig. 10a, the PL emission spectra of pristine g-C₃N₄ and g-C₃N₄-425 exhibit a distinct peak at 455 nm caused by the recombination of photo-generated electrons and holes, which is consistent with variation of the band gap energy [10]. Obvious, the PL intensity of g-C₃N₄-425 is much lower

than that of pristine g-C₃N₄, and the decreased peak intensity further confirms a lower electron–hole recombination rate for g-C₃N₄-425 comparing with pristine g-C₃N₄. Moreover, the charge transfer dynamics for the two products are analyzed by the TRPL decay measurements (Fig. 10b), the average lifetime is calculated using the following relation: $\tau_{av} = a_1\tau_1 + a_2\tau_2 + a_3\tau_3$ (τ_1, τ_2 and τ_3 are the lifetime, a_1, a_2 and a_3 are normalized pre-exponential factors) [3]. The average lifetime (τ_{av}) of g-C₃N₄-425 decreases to 3.96 ns, as compared to that of pristine g-C₃N₄ (8.47 ns). These results imply that a new nonradiative decay pathway may be opened due to the charge transfer through the new channels and the photogenerated carriers of g-C₃N₄-425 are more quickly captured by reactive substrates and thus are able to drive redox reaction [40,45]. Photoelectrochemical measurements are used to further confirm the enhanced excitation and separation of the photo-generated carriers. Fig. 10c shows a comparison of the photocurrent-time curves for pristine g-C₃N₄ and g-C₃N₄-425 with typical on–off cycles under visible light irradiation, the photocurrent response of g-C₃N₄-425 is higher than that of pristine g-C₃N₄ strongly illustrating that the interface charge separation efficiency is improved. Meanwhile, to

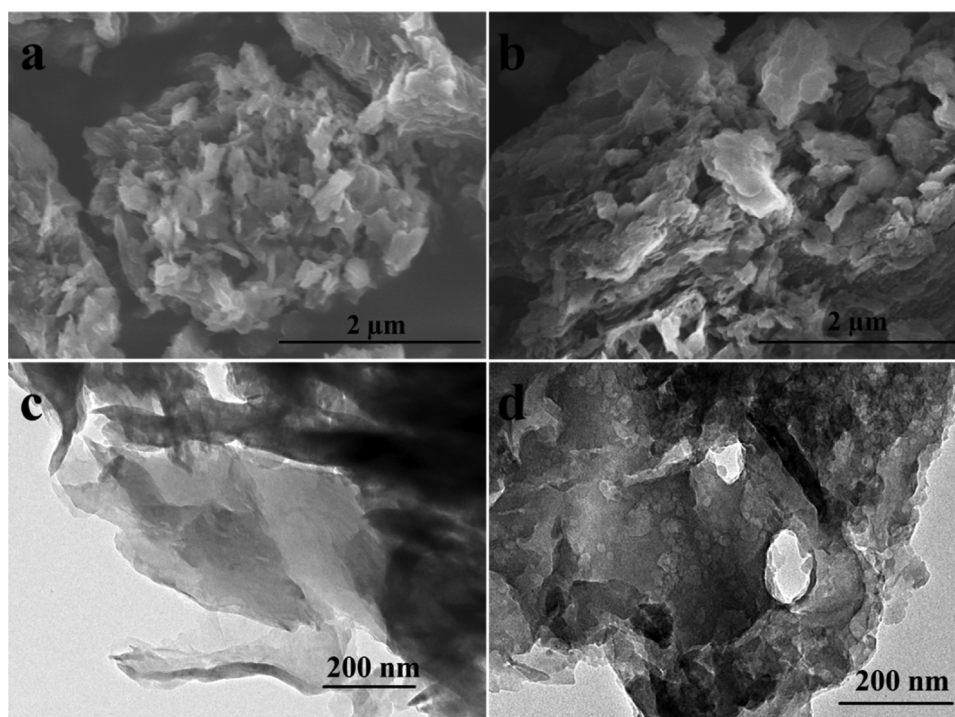


Fig. 8. SEM images of pristine g-C₃N₄ (a) and g-C₃N₄-425 (b), TEM images of pristine g-C₃N₄ (c) and g-C₃N₄-425 (d).

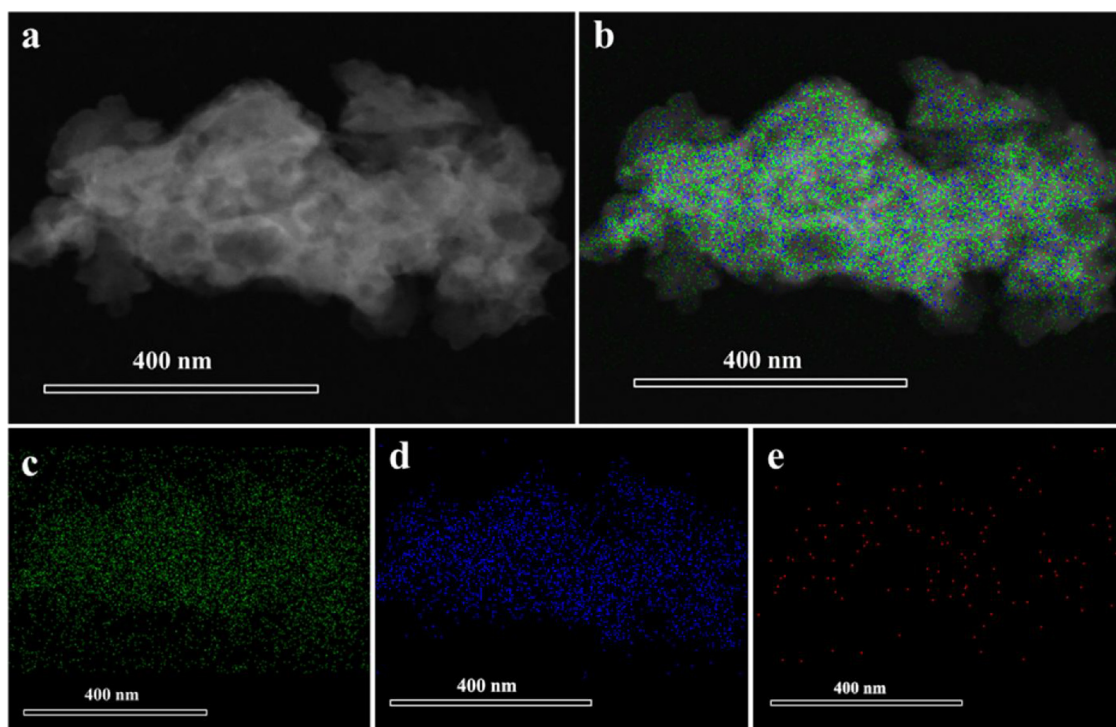


Fig. 9. (a) STEM images of g-C₃N₄-425, (b) mixed EDS mappings of elemental C, N and P in g-C₃N₄-425, (c–e) EDS mappings of elemental C (green dots), N (blue dots) and P (red dots), respectively (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

gain deeper insight into the charge transport behavior of the both products in absence of light excitation, the electrochemical impedance spectroscopy (EIS) measurements were carried out under dark condition. An equivalent electronic circuit model (inset of Fig. 10d) was carried out to simulate the EIS test system, in which the R_s and R_{ct} stood for the total electrolyte solution resistance and the interfacial charge-transfer resistance, respectively. The diameters of the semicircular arc in the EIS Nyquist plots reflect the charge-transfer resistance of the working electrodes. In general, the smaller the diameter of semicircle arc of the EIS spectrum is, the lower the electron-transfer resistance value (R_{ct}) is [46]. Compared with pristine g-C₃N₄, a smaller diameter of g-C₃N₄-425 is observed, indicating a good electronic conductivity in g-C₃N₄-425 sample. According to all of the results, the photo-excited charge carriers of g-C₃N₄-425 can be separated more effectively than that of pristine g-C₃N₄.

In order to investigate the band potentials (VB and CB) of pristine g-C₃N₄ and g-C₃N₄-425, the VB XPS analysis was carried out, the detailed information can be seen in section 7, supporting information. In Fig. S7, the VB maximums of g-C₃N₄ and g-C₃N₄-425 are 1.94 and 1.90 eV, respectively. The valence band potentials of g-C₃N₄ and g-C₃N₄-425 are calculated to be 1.72 and 1.68 eV versus normal hydrogen electrode (NHE) at pH 7 using the formula $E_{NHE} = \Phi + VBM - 4.5$ (E_{NHE} = the normal hydrogen electrode, $\Phi = 4.28$ eV = the work function of the analyzer, namely, the Al metal). According to the formula $E_{CB} = E_{VB} - E_g$, the CB minima of g-C₃N₄ and g-C₃N₄-425 are determined to be -0.88 eV and -0.54 eV, respectively. Based on the above-discussed results, possible mechanism for enhanced photocatalytic H₂ production and CO₂ reduction activities has been discussed in Fig. 11. During the process of heating, NaH₂PO₂ will decompose into gaseous PH₃ and solid-state Na₂HPO₄ at temperature greater than 150 °C. According to the XPS and FTIR spectra analysis, the oxidizing solid-state Na₂HPO₄ can react with terminal amino groups ($-C-NH_2$) to produce cyano groups ($-C\equiv N$) and PH₃ can take part in P doping in g-C₃N₄ system according to the formation of P–N bond. The reduced band gap energy of g-C₃N₄-425 can be seen from Fig. 11, so more visible light can be absorbed to produce more photogenerated carriers. The

photogenerated electrons can transfer to Pt or Au to take part in reduction reaction to produce H₂ or CO, the photogenerated holes can take part in oxidation reaction. As we all know, g-C₃N₄ is a typical n-type material due to containing many terminal amino groups ($-C-NH_2$) as electron donors, the produced cyano groups ($-C\equiv N$) as strong electron-withdrawing groups in g-C₃N₄ system can promote the efficient separation of photo-generated electron-hole pairs, which can be proved by enhanced photocatalytic H₂ production in Fig. 5c. A simple heat treatment with NaH₂PO₂ can bring so many advantages, more photo-excited charge carriers can be produced and separated to take part in the photocatalytic reactions, leading to higher efficiencies in photocatalytic H₂ production and CO₂ reduction.

4. Conclusion

In summary, we developed a simple and effective method to prepare phosphorus and cyano groups ($-C\equiv N$) modified g-C₃N₄ photocatalyst by NaH₂PO₂ treatment at different temperatures in Ar atmosphere. After treatment, the intrinsic 2D layered structure was still maintained, the formation of cyano groups ($-C\equiv N$) can enhance the light absorption and act as strong electron-withdrawing groups, which can promote the efficient separation of photo-generated electron-hole pairs. Meanwhile, P element doping into the g-C₃N₄ system enhances the visible light absorption, decreases the band gap energy, increases the electric conductivity and suppresses the recombination of photo-generated carriers. Together with these advantages, the photocatalytic H₂ production activity of the optimal g-C₃N₄-425 sample is nearly 6.7 times higher than that of pristine g-C₃N₄ and 2.12 times higher than that of g-C₃N₄ owning cyano groups alone, the photocatalytic CO₂ reduction activity of the optimal g-C₃N₄-425 sample is nearly 1.58 times higher than that of pristine g-C₃N₄. This work provides a simple and promising strategy to bring so many advantages to realize the highly effective photocatalytic activity.

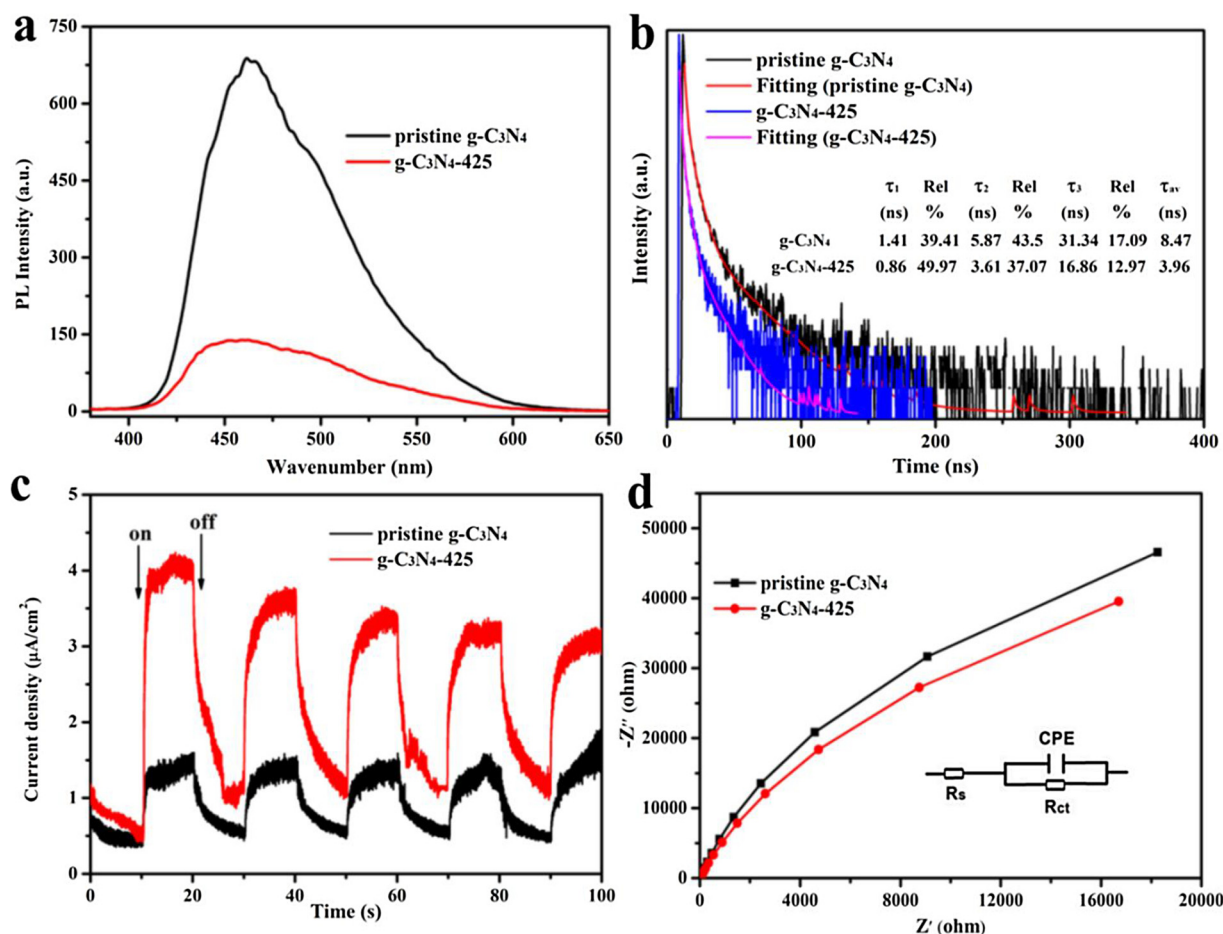


Fig. 10. (a) PL spectra of the pristine g-C₃N₄ and g-C₃N₄-425 samples; (b) TRPL decay spectra of the pristine g-C₃N₄ and g-C₃N₄-425 samples; (c) transient photocurrent responses of the pristine g-C₃N₄ and g-C₃N₄-425 samples in 0.2 M Na₂SO₄ aqueous solution with AM1.5 as light source; (d) EIS plots of the pristine g-C₃N₄ and g-C₃N₄-425 samples in 0.2 M Na₂SO₄ aqueous solution under standard solar simulator (AM 1.5) irradiation.

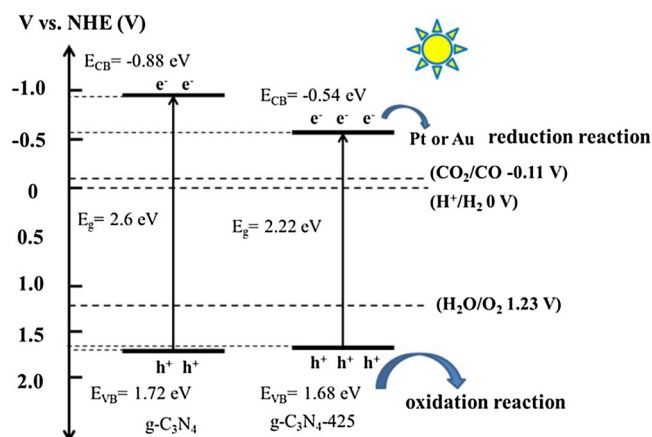


Fig. 11. Schematic illustration of the charge separation and transfer in g-C₃N₄ and g-C₃N₄-425 system during the photocatalytic H₂ production and CO₂ reduction.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.apcatb.2018.03.094>.

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